Closely diffusing O–H, amide N–H and methylene C–H oscillators quench the excited state of europium complexes in solution

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In octadentate complexes of europium(III) based on 1,4,7,10-tetraazacyclododecane, deuteriation studies and measurements of excited state lifetimes in solution reveal that amide N–H and methylene C–H oscillators afford an intramolecular vibronic deactivation pathway of the excited Eu $^5D_0$ emissive state which, coupled with a reassessment of the effect of intermolecular OH oscillator quenching, allows more accurate estimates of complex solvation state, *q*, to be made.

It has been appreciated for some time that energy transfer from the excited state of europium complexes to proximate O–H oscillators affords an effective non-radiative de-excitation pathway that is absent in D_2O.[1] In general, the rate constant for depopulation of the europium excited state in water may be partitioned as the sum of the different quenching contributions [eqns. (1)–(3)]:

$$k_{H_2O} = k_{nat} + k_{nr} + \Sigma k_{XH} \quad (1)$$

$$k_{D_2O} = k_{nat} + k_{nr} \quad (2)$$

$$k_{H_2O} - k_{D_2O} = \Sigma k_{XH} \quad (3)$$

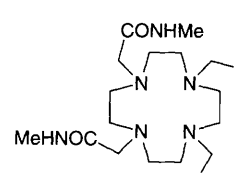
where k_{nat} is the natural radiative rate constant, k_{nr} is the rate constant for non-radiative de-excitation and Σk_{XH} is the sum of the rate constants for energy transfer to proximate energy matched XH oscillators. Knowing the contribution of each water molecule to this difference in rates and neglecting all other contributions, this analysis has been used to estimate the apparent hydration state, *q*, of a europium complex in solution, by measuring the excited-state lifetime (τ) in H_2O and D_2O [eqns. (3) and (4)],[2] where $k = 1/\tau$ = the rate constant for depopulation of the excited state.

$$q = 1.05(k_{H_2O} - k_{D_2O}) \quad (4)$$

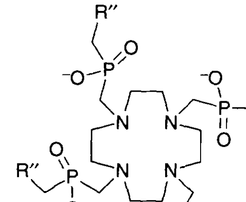
In the polydentate ligands L^1 (dota[3]),† L^2 (refs. 4 and 5) and L^3 (ref. 6) that are known to form kinetically stable europium(III) complexes, there are other oscillators that may quench the europium excited state. Given that the vibrational stretching frequency of amide N–H {*e.g.* ν_{NH} in $[EuL^{2a}]^{3+}$ is 3310 cm^{-1}} and methylene C–H bonds ($\nu_{CH} \approx 2950$ cm^{-1}) are somewhat similar to those of an O–H group ($\nu_{OH} \approx 3400$ cm^{-1}), then it might be expected that higher lying vibrational levels of such oscillators may be fairly close in energy to the Eu $^5D_0$ state. For an OH oscillator, it is to the third vibrational level that energy transfer from the proximate europium centre is reputed to occur. The corresponding O–D, N–D and C–D oscillators have much lower stretching frequencies and any energy matching is only possible with higher vibrational states for which the Franck–Condon overlap factor is unfavourable. Overall, X–D oscillators are at least 200 times less effective at vibronic quenching than the corresponding X–H oscillators.[1b]

The europium complex of the tetrabenzylphosphinate, L^{3a}, by analogy with the isostructural yttrium and gadolinium complexes,[6] does not possess a metal-bound water molecule, and in the crystal lattice the nearest water molecule is some 5.6 Å distant from the bound metal centre. The difference in *k* values measured in H_2O and D_2O, (equivalent to an apparent *q* value[2] of 0.16, Table 1) therefore must represent the quenching contribution of unbound water molecules, *i.e.* those water molecules that are freely diffusing close enough to the Eu ion to cause some vibrational quenching over a longer distance. The related europium–tetramethylphosphinate complex, $[EuL^{3b}]^-$, is much less hydrophobic {log *P* values (octanol–water) of the corresponding Gd complexes are −4.75 for $[Gd^{3b}]^-$ and −0.66 for $[Gd^{3a}]^-$} and NMRD studies[6] indicate that in the less sterically demanding $[GdL^{3b}]^-$ the nearest diffusing water molecule is 0.42 Å closer to the metal centre than in $[GdL^{3a}]^-$. The *q* value estimated for $[EuL^{3b}]^-$ is 0.27, highlighting the sensitivity of the variation of energy transfer with distance.‡ Thus intermolecular energy transfer to proximate OH oscillators will contain a component due to *unbound* but closely diffusing water molecules, in addition to a term for each *bound* water molecule.

Protium/deuterium exchange at amide NH in the europium complexes of L^{2a} and L^{2b} takes place rapidly at pD 6 (293 K) and was confirmed by ^1H NMR analysis. The europium centre acts as an effective charge sink and thereby promotes amide enolisation[7] (Scheme 1). Exchange of the methylene hydrogens in the acetate groups of the $[EuL^1]^-$ complex does not occur at ambient temperature and pH, but proceeds readily at higher pH. With this europium complex of dota, the precise percentage of deuterium incorporation was assayed by negative ion ESMS and the value was compared to that obtained by ^1H NMR analysis of the residual shifted diastereotopic C–H resonances at δ −16.4 and −18.1 (293 K, pD 6). After heating to 60 °C for 18 h at pD 11, 90(2)% deuterium incorporation was obtained, *i.e.* an average 7.2 of the 8 methylene C–H protons had undergone exchange. H/D exchange in the benzylic positions of L^{3a} was achieved by treating the corresponding tetraester with CD_3OD–CD_3ONa, and 87(3)% D incorporation was measured



L^1 dota

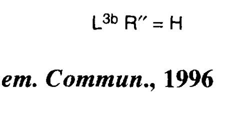


L^{2a} R = Me, R′ = H

L^{2c} R = R′ = H

L^{2d} R = R′ = Me

L^{2b} R = CH_2Np, R′ = H



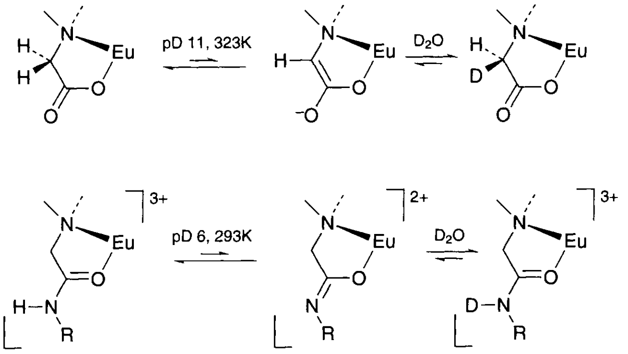
L^{3a} R″ = Ph

L^{3b} R″ = H

Table 1 Rate constants for depopulation of the excited states of europium complexes[a] and the effect of H/D exchange [293 K; k values were reproducible to ±0.03 $(ms)^{-1}$]

	k_{H_2O}	k_{D_2O}	Δk	Mean contribution per XH oscillator $(s^{-1})^{b,c}$ (±20%)		
Complex		$(ms)^{-1}$		Σ_{OH}	NH	CH
$[EuL^{3a}]^{-b}$	0.63	0.48	0.15	75	—	~5
$[Eu\{[^2H_7]\text{-}L^{3a}\}]^-$	0.60	0.44	0.16	80	—	
$[EuL^{3b}]^-$	0.80	0.54	0.26	130		
$[EuL^1]^-$	1.60	0.54	1.06	530	—	26
$[Eu\{[^2H_7]\text{-}L^1\}]^{-d}$	1.41	0.36	1.05	525	—	
$[EuL^{2a}]^{3+}$	1.82	0.47	1.35	525	75	—
$[EuL^{2b}]^{3+e}$	1.72	0.42	1.30	525	63	—
$[EuL^{2c}]^{3+c}$	1.93	0.46	1.47	525	53	—
$[EuL^{2d}]^{3+}$	1.60	0.54	1.06	530	—	

[a] NMR and luminescence studies show that for the europium complexes of L^1, L^{2a}, L^{2b}, L^{3a} and L^{3b} there is one (>90%) major diastereoisomer present in solution. [b] X-Ray analysis shows that there is no bound water molecule (nearest water is 5.62 Å away).[6] The Σ_{OH} term refers to an estimate of the sum of the quenching contributions of both the nearest diffusing OH oscillators and those OH oscillators due to any metal-bound water molecule, normalised to one OH oscillator. There was 87(3)% H/D exchange in the benzylic positions of $[EuL^{3a}]^-$ after H/D exchange. [c] Data from ref. 5: one metal-bound water molecule was revealed by X-ray analysis. The two diastereotopic amide NH (like the methylene CH) oscillators have different IR stretching frequencies and are expected to differ in their ability to quench the europium excited state. [d] $[Eu(dota)]^-$ possesses one bound water molecule.[3] The extent of deuterium incorporation[90(2)%] was assessed by negative ion ESMS and ^1H NMR analysis. [e] The corresponding more hydrophobic tetranaphthylamide gave values of k = 1.69 (H_2O) and 0.42 $(ms)^{-1}$ (D_2O).



Scheme 1

by NMR and confirmed by −ESMS analysis of the europium complex.

Measurements of the excited-state lifetime of the unexchanged and H/D exchanged europium complexes of L^1, L^2 and L^3 in H_2O and D_2O were made (Table 1). Given that $[EuL^1]^-$ and $[EuL^{2c}]^{3+}$ are known to possess one bound water (q = 1), from crystallographic and solution NMRD analyses of the corresponding gadolinium complexes,[3,5] while $[EuL^{3a}]^-$ possesses no 'inner sphere' water molecule, the relative contribution of the NH and CH oscillators to the quenching of the europium excited state can be assessed. This quenching effect will, of course, be a sensitive function of the distance between the given XH oscillator and the europium centre. Assuming that each 'inner sphere' OH oscillator contributes roughly 450 s^{-1} to the rate of depopulation of the excited state, a coordinated amide NH is less efficient (*ca.* 75–55 s^{-1}) and a methylene C–H has the least effect (*ca.* 25 s^{-1}).§ The sum of these individual contributions can be quite significant: in $[EuL^{2c}]^{3+}$, for example, a solution q value of 1.5 was estimated[5] recently, but the sizeable contribution of the amide N–H oscillators (Table 1) was ignored. In the case of deuteriated $[EuL^{3a}]^-$, the lack of any large effect may be ascribed at least in part to the greater distance between the CH_2 oscillators and the metal centre (*ca.* 0.7 Å from the reported crystal structures[6,8]) comparing $[EuL^{3a}]^-$ with $[EuL^1]^-$.

In summary, in allowing for the quenching rôle of all exchangeable X–H oscillators in europium complexes, and taking note of the relative contributions of both bound and closely diffusing water molecules, more accurate estimates of complex hydration state may be gained. Furthermore, given the ease of certain CH/CD substitutions, europium (and terbium) complexes with significantly longer-lived excited-state lifetimes (and higher quantum yields) may be obtained. This is important in the development of their use as long-lived luminescent labels in biological assays.

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Footnotes

† dota, L^1, is 1,4,7,10-tetraazacyclododecane tetraacetate

‡ The distance dependence of vibronic quenching, coupled with the good correlation of q(Eu) and NMRD derived Gd–**H**–OH distances,[4] highlights the fact that for $q < 1$, partial hydration states occur, *i.e.* there is a spectrum of $M \cdots OH_2$ distances wherein $q = 0$ and $q = 1$ represent boundary conditions.

§ That CH/D substitution affects excited-state lifetimes has been noted:[1a] $[Eu(MeCO_2)_3]$, $k(D_2O)$ = 0.56 $(ms)^{-1}$; $[Eu(CD_3CO_2)_3]$, $k(D_2O)$ = 0.42 $(ms)^{-1}$, *i.e.* Δk = 140 s^{-1} as a result of the quenching effect of the six CH oscillators in the likely major aquo species, $[Eu(OAc)_2(H_2O)_5]^+$.

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